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CHEMICAL ORIGIN OF THE VENUSIAN CLOUDS

By: R. C. Robbins

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Introduction

This project is a laboratory study of chemical reactions which may occur in the atmosphere of Venus. Because Venus lacks a magnetic field, solar hydrogen must react with the components of the high atmosphere of Venus as the the solar wind penetrates the atmosphere.

The reactions being investigated in this program are:

$$H^* + CO \rightarrow \text{products} \qquad (1)$$

$$H^* + CO_2 \rightarrow \text{products} \qquad (2)$$

$$H^* + CO + CO_2 \rightarrow \text{products} \qquad (3)$$

$$H^* + CO + N_2 \rightarrow \text{products} \qquad (4)$$

$$H^* + CO + CO_2 + N_2 \rightarrow \text{products} \qquad (5)$$

In their studies of the reaction of $H(^2P)$ with N_2, Tanaka and McNesby[1] found ammonia to be the only product. They measured rates of ammonia formation in a number of experiments, and from their data we have estimated a rate coefficient of 10^{-15} cc molecule^{-1} sec^{-1} for the primary reaction between H* and N_2.

If, under the conditions found in the high Venus atmosphere, solar hydrogen does indeed react to a significant extent with the CO, CO_2, and N_2 present, radicals containing oxygen-hydrogen carbon-hydrogen, and nitrogen-hydrogen bonds will be produced. If photolysis of the primary reaction products is inhibited, these radical species will condense and polymerize to form water, hydrocarbons, and amino compounds. Large amounts of condensed products accumulating from this source could produce the observed permanent cloud layer in the Venusian atmosphere.

The reactions were studied in a flow system in which ground-state hydrogen atoms were irradiated with Lyman-α and then mixed with the reactant or combination of reactants. After the gas mixture passed through a dark reaction chamber, the condensable products were collected in a cold trap. The collected material was then analyzed by gas chromatography.

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[1] Tanaka, I. and J. R. McNesby, J. Chem. Phys. 36, 3170-73 (1962).

We found that the reaction between excited hydrogen atoms and carbon monoxide yields intermediate radical and atom species which undergo rapid secondary reactions to produce water and organic compounds. The principal organic compounds formed are ethylene, formaldehyde, and glyoxal, all readily polymerizable substances. Since the reaction course proceeds in this fashion under laboratory conditions, with the formation of these reactive monomers, it is altogether possible that the same reactions and products could be important in the high Venus atmosphere.

A detailed qualitative and quantitative analysis of the products was made. On a mole basis the products were 70% water and 30% organic compounds. The chromatograph showed 13 organic peaks of which five were positively identified, four tentatively identified, and four unknown. Half of the organic product was ethylene; two other major organic components were formaldehyde and glyoxal. In addition, methanol, ethane, acetylene, propylene, acetaldehyde, acetone, ethanol, and formic acid were positively or tentatively identified as being present. Acetaldehyde, if present, appeared at the same time as formaldehyde; ethanol and formic acid peaks were broad, difficult to analyze, and they interfered with the methanol peak.

Water was determined by passing the product gases through a heated calcium carbide (CaC_2) cartridge and then measuring the acetylene formed with the flame ionization detector.

A comparison of the water/organic product ratio (70/30) with the heats of reaction ($\triangle H$) of the two reactions,

$$H(^2P) + CO \rightarrow OH + C \qquad (6)$$

$$H(^2P) + CO \rightarrow CH + O \qquad (7)$$

is of interest. Reaction (6) is the water-producing reaction; it is exothermic by 75 kcal/mole. Reaction (7) is the organic-producing reaction; it is exothermic by 60 kcal/mole.

In view of the nature and distribution of the products, the two second-stage reactions which are probably most important are

$$OH + H_2 \rightarrow H_2O + H \qquad (8)$$

$$CH + H_2 \rightarrow CH_2 + H \qquad (9)$$

The relatively large amount of ethylene produced is of theoretical interest in regard to the Venus atmosphere, because a significant production rate of ethylene provides the initial condition for making stable polymeric compounds. Such polymers may be present in the Venusian cloud layer.

Summary

Although reaction (1), $H^* + CO \rightarrow$ products, is fast and efficient and yields large amounts of OH and CH radicals, the reaction is sensitive to the presence of other gaseous components. Carbon dioxide was found to have a marked negative effect on the production of organics. The presence of excess molecular nitrogen, on the other hand, appears to promote the production of organics. Almost certainly the CO_2 competes directly with the CO in reacting with the H*, but the enhancement role of the N_2 is not yet understood.

These are both important effects, and the possible magnitude of these divergent factors on the production of organic molecules in the high Venus atmosphere requires more investigation.

Experimental Procedure and Discussion

Reaction (2), $H^* + CO_2 \rightarrow$ products, was investigated during this report period. No organic products were collected. This complete abscence of hydrogen-carbon bond formation probably defines the entire reaction course; the primary reaction could have two sets of products, i.e.,

$$H^* + CO_2 \rightarrow OH + CO \qquad (2a)$$

or

$$H^* + CO_2 \rightarrow CH + O_2 \qquad (2b)$$

Reaction (2b) is of no importance, since no hydrocarbons are produced and the primary reaction products are OH and CO. In the laboratory, the OH radical then reacts with H_2 and CO to end the condensable product reaction sequence. The reaction proceeds as follows:

$$OH + H_2 \rightarrow H_2O + H \qquad (4)$$

$$OH + CO \rightarrow CO_2 + H \qquad (6)$$

However, in the high atmosphere of Venus, OH must follow a different reaction route, first

$$OH + CO \rightarrow CO_2 + H \quad (6)$$

and less important

$$OH + OH \rightarrow H_2O + O \quad (7)$$

When CO_2 is added to the H* + CO system, reaction (3), it is extremely effective in increasing the water/organic product ratio via reaction (2a). One part CO_2 per ten thousand CO caused a 20 to 30 percent reduction in the organic yield. On the other hand, when nitrogen is added to the H* + CO system, reaction (4), it appears to have a small, positive effect on the production of organic compounds. The mechanism for this effect is not obvious, but the nitrogen must directly alter the H* + CO reaction course in some manner. When both CO_2 and N_2 are added to the H* + CO system, reaction (5), the CO_2 inhibiting effect strongly overrides the N_2 enhancement effect on the production of organics.

Both of these effects are probably important in the high atmosphere of Venus. Most of the gas present at 200 km is molecular nitrogen, while the steady-state concentration of CO_2 is very small. However, the CO_2 concentration may be large enough to strongly inhibit the production of organic precursors by means of the H* + CO $\rightarrow$ products reaction.

In addition to the investigations of the effects of CO_2 and N_2, experiments were made using a small concentration of CO in argon. More experiments must be made with argon mixtures, as the data were inconclusive.

Future Work

Attempts will be made to calculate reaction rates by changing the reaction volumes for the various reactant combinations. The argon diluent system will also be used. Photolysis effects will be studied by adding a photolysis chamber immediately downstream from the Lyman-α irradiation chamber.

R C Robbins /CJS
R. C. Robbins, Senior Physical Chemist
Atmospheric and Environmental
Sciences Group

Approved:

Charles J. Cook
Charles J. Cook, Executive Director
Chemical, Theoretical, and Applied Physics